

# Controlled arsenic diffusion in epitaxial $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ layers in the evaporation–condensation–diffusion process

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## Abstract

The results of controlled doping of  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  epitaxial layers are presented. The investigated layers were obtained by the evaporation–condensation–diffusion method in the process of isothermal growth. The process of auto diffusion from the solid phase was investigated. This process consists in the diffusion of As dopants from CdTe substrate into the grown epitaxial layer. Two types of CdTe substrates, uniformly doped in the process of synthesis and unalloyed with ion implanted surface layer, have been used as sources of As diffusant. Comparative analysis of galvanomagnetic measurements and SIMS spectra was carried out. The results of investigations indicate the very high, almost 100%, electrical activity of As dopants in the  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  epitaxial grown layer. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

$\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  solid solutions with  $x=0.2$ – $0.3$  are widely used as semiconductor materials for manufacturing infrared photodetectors for the 3–5- and 8–14- $\mu\text{m}$  spectral range. For now many investigations have been concerned with the study of dopants diffusion in  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  epitaxial layers obtained by LPE [1,2], MBE [3–5] and MOVPE [6–8]. Detailed analysis of doping processes of V group elements [9–11] shows the amphoteric nature of these dopants. From the thermodynamical conditions of the growth (which homogeneity region Te- or Hg- is closer) it follows that dopant could be introduced either to metallic or chalcogenide sublattice this way acting as donor or acceptor. An intensive search of manufacturing the p-type doped material mostly focused on the usage of As as the most perspective dopant. The most important reason for this is that As

has low diffusivity and high doping levels ( $\sim 10^{17}$  to  $10^{19} \text{ cm}^{-3}$ ) could be obtained [12]. Experiments on controlled doping with As during the  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  epitaxial growth by modified ISOVPE evaporation–condensation–diffusion method [13] were performed. Two substrates for  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  ECD growth were used:

- doped (111) CdTe monocrystals grown by the Bridgman method where As was introduced during synthesis ( $n_{\text{As}} \sim 10^{16}$  to  $10^{17} \text{ cm}^{-3}$ ); and
- undoped (110) and (111) CdTe monocrystals on the surface of which the controlled quantity of As was introduced by ion implantation.

## 2. Experimental details

The use of CdTe substrate as a dopant source, which is determined by controlled doping processes, raises certain requirements for the quality of its surface preparation. For a consequent preparation of working surfaces non-abrasive two-side chemical–mechanical polishing

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Table 1  
Results of electrophysical measurements for  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  epitaxial layers

Sample no.	Dopant source	$x$	$d$ ( $\mu\text{m}$ )	Conductivity type	$\mu$ ( $\text{cm}^2/\text{Vs}$ )		$R$ ( $\text{cm}^3/Q$ )		$N_a - N_d$ , $\text{cm}^{-3}$
					273 K	77 K	273 K	77 K	
V-13	Substrate	0.22	51	P	58	218	13.6	65	$9.6 \times 10^{16}$
V-14	Substrate	0.23	53	P	455	234	146	66	$9.6 \times 10^{16}$
V-17	Substrate	0.19	66	P	6750	232	650	98	$6.4 \times 10^{16}$
V-29	Vapor phase	0.28	50	N	4600	7500	70	80	$7.8 \times 10^{16}$
73-1	Implanted	0.22	65	N	10 340	5210	110	180	$1.3 \times 10^{16}$
73-2	Substrate	0.21	70	P	3741	150	293	464	$1.35 \times 10^{16}$
73-3	Substrate	0.20	68	P	9283	325	589	465	$1.35 \times 10^{16}$
74-1(111)	Implanted	0.17	90	P	12 400	32 450	80	198	$3.17 \times 10^{16}$
77-1(111)	Implanted	0.26	67	P	5290	418	843	368	$1.7 \times 10^{16}$
77-2(110)	Implanted	0.24	67	P	5850	329	562	518	$1.2 \times 10^{16}$
70-4	Non-doped	0.22	52	N	7232	34297	417	840	$7.4 \times 10^{15}$

have been used, which allow us to obtain the parallel-sided substrate surfaces with minimal depth of improper layer. Just before loading them into ampoules for use as doped substrates (or a crystal holder in the case of ion beam implantation to non-doped substrates) final etching in 4% bromine butanol solution was carried out. Surfaces of prepared undoped CdTe substrates were implanted with As ion beam with energy  $E=100$  keV and dose  $D=5 \times 10^{14}$  to  $1 \times 10^{16}$   $\text{cm}^{-2}$ . Implantations were carried out using 'Balzers' MPB-202 ion-beam device. Quartz ampoules and fittings were used for epitaxial layer growth. Synthesized HgTe single crystals after chemical etching in bromine etchants were used as a source. Prepared quartz ampoules were loaded with substrates, sources and liquid mercury. Sizes and shapes of ampoules and quartz fittings were the same in all experiments. The mounted ampoules were placed in a vacuum with an oil-free exhaust system, soldered up and loaded into a two-zone resistive heater furnace preheated to the required temperature. Temperatures were measured with thermocouples mounted on the quartz ampoule in the source and substrate zones and in the liquid mercury zone. The growth zone temperature was  $600^\circ\text{C}$  in all experiments while the mercury zone temperature was kept level resulting in  $P_{\text{Hg}}=2-4$  standard atmospheres. Post-growth annealing of epitaxial layers in a saturated mercury pressure was carried out at  $320/300^\circ\text{C}$  during 60 h to reduce mercury vacancy concentration. The epitaxial layer thickness was determined on the cleaved cross-sections by a metallurgical microscope. The samples for this measurement were etched in advance in the selective etchant on the basis  $\text{H}_2\text{O}/2\text{H}_2\text{O}_2/3\text{HF}$  with the aim of maximum Hg penetration in to the CdTe substrate during ECD epitaxial growth. The thickness measured in such a way is the total thickness of the grown epitaxial layer and interdiffusion region. The substrate thickness in our experiments was 1–2 mm, so the diffusion front of the main components during the epitaxial process did not reach the backside of the substrate. The composition of

$\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  epitaxial layers on the surface was determined after unloading by measuring the cut-off of the optical absorption. The conductivity type and free carrier concentration were determined by galvanomagnetic measurements at 77–300 K and 0.01–1.8 T magnetic field ranges. The results of measurements are presented in Table 1. Secondary ion mass spectroscopy (SIMS) on a 'Cameca' IMS-6F device was used to define the As distribution on sample depth.

### 3. Results and discussion

The search of a effective method of  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  doping with As during ECD epitaxy was carried out in different directions. Attempts to induce doping from the vapor phase using As portions dissolved in mercury were made. As a result n-type layers with high concentration and low carrier mobility (sample V-29, Table 1) were obtained. This could be caused by the fact that growth regimes were near to Te-enriched solid solution homogeneity area [14], so As is embedded into the metallic sublattice and acts as a donor. The use of CdTe as an As source during the VPE from metal to organic compound epitaxy of  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  by interdiffusion multilayer process (IMP-MOVPE) [6,7] as well as ISOVPE of tetradic epitaxial layers  $\text{Hg}_{1-x-y}\text{Cd}_x\text{Mn}_y\text{Te}$  on the  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$  substrates show that CdTe could be used for solid phase doping during ECD epitaxial growth of  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ . In our experiments on  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  epitaxial layer growth on As uniformly doped during synthesis, CdTe substrates p-type epitaxial layers were obtained. The carrier concentration of layers corresponds to doping concentration of substrate. So, doping concentration of substrate was  $n_{\text{As}} \sim 10^{17} \text{cm}^{-3}$  for samples V-13, V-14, and V-17 and  $n_{\text{As}} \sim 10^{16} \text{cm}^{-3}$  for samples 73-2 and 73-3. Fig. 1 shows the obtained SIMS method distribution of As on the depth of epitaxial layers grown on uniformly doped substrates for the 73-3 sample. It should be pointed out that if non-doped substrates are used, the n-type epitaxial layers with parameters such

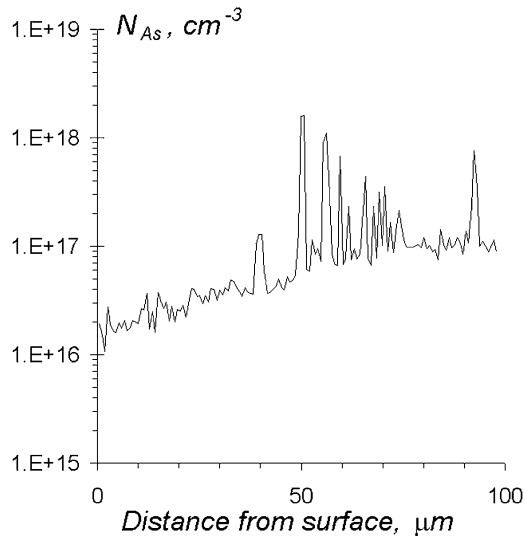


Fig. 1. As SIMS — distribution of the thickness of epitaxial layer for 73-3 sample (doping source — uniformly doped CdTe substrate).

as those presented in Table 1 for the 70-4 sample are obtained under the same growth and post-growth treatment conditions.

In the following experiments attention was focused on ion beam implantation as a technique that ensures control of the implanted dopant quantity over a wide range, thus enabling more controlled processes of  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  doping. The same ion energy  $E=100$  keV was used for As ion implantation into undoped CdTe substrates. CdTe substrates were mounted into quartz ampoules and loaded to a furnace immediately after ion beam implantation. Sample CdTe (111) with an As implanted dose of  $D=5 \times 10^{15} \text{ cm}^{-2}$  was used as a substrate for deposition of epitaxial layer in 74-1. The measured electrophysical properties of this sample are shown in Table 1 and distribution of dopant on the thickness of epitaxial layer in Fig. 2. Epitaxial layers in samples 77-1 and 77-2 were grown on CdTe substrates with different crystal orientations [(111) and (110), respectively] but with the same implanted arsenic dose  $D=1 \times 10^{15} \text{ cm}^{-2}$ . As can be seen from Table 1, the carrier concentrations do not differ greatly, i.e. the influence of crystallographic orientation on the epitaxial layer doping during ECD growth is not significant. The results in comparison show the correlation between the carrier concentration in the epitaxial layer and the concentration of implanted arsenic. Up-diffusion of dopant in CdTe substrate was carried out before growth after arsenic ion beam implantation with  $D=1 \times 10^{15} \text{ cm}^{-2}$  to estimate the influence of improper layers on the ECD process of epitaxial growth. Up-diffusion was carried out by annealing during 5 min in Cd vapor under growth temperature to heal the radiative defects. The layer with  $\sim 1 \mu\text{m}$  thickness after treatment was

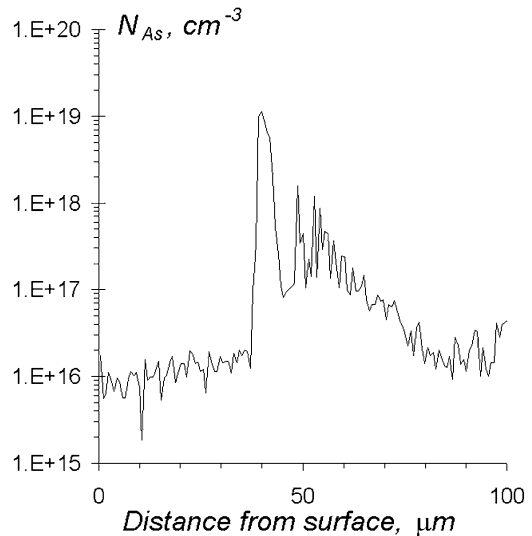


Fig. 2. As SIMS — distribution of the thickness of epitaxial layer for 74-1 sample. Preliminary up-diffusion of dopant was not carried out.

chemically etched from the surface and the substrate was loaded into the ampoule for the growth process.

The  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  epitaxial layer (sample 73-1) was grown on the substrate prepared using this technique. The measured electrophysical properties of this sample are shown in Table 1 and the distribution of dopant on the thickness of the epitaxial layer in Fig. 3. The experiment carried out allows us to conclude that radiation defects which arise from ion beam implantation are healed during the starting phase of the epitaxial growth and do not have much influence on the dopant diffusion process. Apparently, the peaks of maximal As concentration which are seen in Figs. 1 and 2 correspond

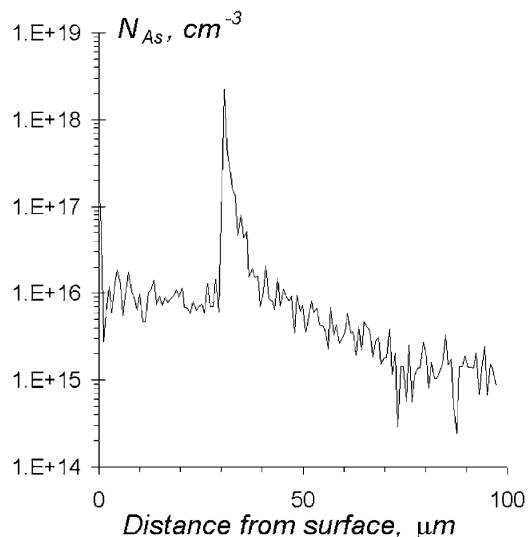


Fig. 3. As SIMS — distribution of the thickness of epitaxial layer for 73-1 sample. Preliminary up-diffusion of dopant in Cd vapor was carried out.

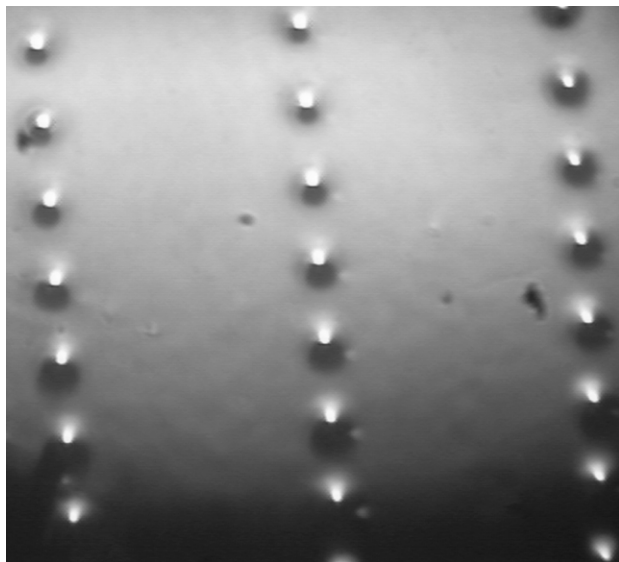


Fig. 4. Photograph of relief of the epitaxial layer  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  grown by ECD.

to the position of the initial surface of the substrate where the epitaxial growth takes place. Study of the interdiffusion process influence on the charged dopant diffusion during epitaxial growth that results in formation of graded-band-gap  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  layers (influence of the internal electric field caused by space inhomogeneity of semiconductor band gap) will be presented in future publications.

The advantages of ion beam implantation which consist of short projection ranges and the possibility of implanting dopant locally have been used to manufacture photovoltaic structures during the epitaxial growth.

The periodical structures,  $80 \times 80 \mu\text{m}^2$ , with period of  $280 \mu\text{m}$  were created by photolithography on the ion beam implanted ( $D=5 \times 10^{14} \text{ cm}^{-2}$ ) CdTe substrate. The surface with relief was obtained after chemical removal of photoresist-free substrate in bromine-free agent up to  $1.5 \mu\text{m}$  in depth. The prepared substrate was mounted in to an ampoule and loaded into the

furnace for epitaxial growth. The photograph of the obtained epitaxial structure is shown in Fig. 4.

#### 4. Conclusions

The electrophysical properties of  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$  epitaxial layers obtained on the ion beam implanted CdTe substrates are defined by the implanted As dose. The influence of substrate crystallographic orientation on the epitaxial layer doping during ECD growth is not significant. The radiation defects which arise from the ion beam implantation heal during the starting phase of the epitaxial growth and do not significantly influence the dopant diffusion process and quality of obtained layers. The possibility of manufacturing graded-band-gap photovoltaic structures during epitaxial growth has been shown.

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